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(21) International Application Number: PCT/GB98/02079 (22) International Filing Date: 15 July 1998 (15.07.98) (30) Priority Data: 9714880.3 15 July 1997 (15.07.97) GB (71) Applicant (for all designated States except US): RHODIA LIMITED [GB/GB]; Oak House, Reeds Crescent, Watford, Hertfordshire WD1 2QH (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): ROBERTS, Neil, Andre [GB/GB]; Rhodia Limited, St. Andrews Road, P.O. Box 46, Avonmouth, Bristol BS11 9YF (GB). (74) Agents: ELLIS-JONES, Patrick, George, Armine et al.; J.A. Kemp & Co., 14 South Square, Gray's Inn, London WC1R 5LX (GB).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: REFRIGERANT COMPOSITIONS (57) Abstract Refrigerant compositions are disclosed which comprise: (a) pentafluoroethane, octafluoropropane, trifluoromethoxydifluoromethane or hexafluoro-cyclopropane, or a mixture of two or more thereof, in an amount from 5 to 60 % based on the weight of the composition, (b) pentafluoroethane, 1,1,1,2- or 1,1,2,2-tetrafluoroethane, 1,1-difluoroethane, trifluoromethoxypentafluoroethane, 1,1,1,2,3,3,3-heptafluoropropane or 1,1,1,2,2,3,3-heptafluoropropane, or a mixture of two or more thereof, in an amount from 30 to 94 % by weight based on the weight of the composition and (c) an unsubstituted hydrocarbon of the formula C_nH_m in which n is at least 4 and m is at least $2n-2$, other than methyl propane, in an amount from 1 to 10 % by weight based on the weight of the composition.		

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REFRIGERANT COMPOSITIONS

10 The present invention relates to refrigerant compositions, particularly for use as replacements in refrigeration equipment currently employing, or designed to employ, the refrigerants R12 and R22.

15 Refrigerant R12 (CCl_2F_2) has been a commonly used refrigerant especially in domestic refrigerators. However, R12 contains chlorine atoms and has been implicated in environmental damage to the ozone layer. As a result efforts have been made to replace R12 with a refrigerant formulation which does not involve the use of refrigerants such as R12 which contain chlorine atoms. Similar comments apply to R22
20 which is used principally for air conditioning systems.

Among alternatives, particular attention has been directed at R134a ($\text{C}_2\text{H}_2\text{F}_4$; 1,1,1,2-tetrafluoroethane) along with pentafluoroethane (R125) (b.pt. -48.6°C). Commercial
25 formulations of these two refrigerants involve the use of a hydrocarbon, namely propane, propylene or isobutane. While these refrigerant formulations are generally effective as replacements for R12 and R22, nevertheless it has been found that their use is not entirely satisfactory.

Difficulty has arisen with the flammability of the
30 fractionated composition, that is to say the vapour above the liquid composition possesses flammability problems. As a result these commercial formulations can produce flammable compositions under some leak scenario conditions. The flammability of these refrigerant compositions resides in their
35 hydrocarbon content. One of the purposes of incorporating the hydrocarbon is so that formulation is compatible with the lubricants ordinarily used in R12 and R22 refrigeration equipment. The specific hydrocarbons have been selected because they possess the correct boiling point in relation to
40 that of the fluorocarbon.

It has now been found, surprisingly, according to the present invention, that if a hydrocarbon with at least 4 carbon atoms other than methyl propane (isobutane) is used instead of

those previously advocated the flammability of the fractionated composition is greatly reduced. This result is very surprising as n-butane, for example, has a significantly higher boiling point (-0.5°) than, say, isobutane (-11.7°C) and is accordingly less volatile. Indeed, the U.S. NIST (National Institute of Standards & Technology) computer programs REFPREP and REFLEAK have predicted that a particularly preferred such n-butane-containing formulation would be flammable when it has been found not to be. Further, although there can be a considerable boiling point range between the lowest boiling point component and the hydrocarbon of the composition the temperature glide of the blend is relatively small. In a particular embodiment, although the boiling point range is 36.2°C, the temperature glide is only 3.9K at the boiling point of -34.6°C at one atmosphere pressure. It is further surprising that such a formulation has a reduced flammability because n-butane, for example, has a larger range of flammability limits as compared with isobutane. Thus n-butane has a flammability range from 1.5 to 10.1% v/v whereas for isobutane it is only 1.7 to 9.7% v/v.

According to the present invention there is provided a refrigerant composition which comprises

- (a) R125, R218 (octafluoropropane; b.pt. -36.7°C), trifluoromethoxy-difluoromethane (b.pt. -34.6°C) or hexafluoro-cyclopropane (b.pt. -31.5°C), or a mixture of two or more thereof, in an amount from 5 to 60% by weight based on the weight of the composition
- (b) R125, R134a, R134 (1,1,2,2-tetrafluoroethane), 1,1-difluoroethane (R152a; b.pt. -24.7°C), trifluoromethoxypentafluoroethane (b.pt. -23.3°C), 1,1,1,2,3,3,3-heptafluoropropane (R227ea; b.pt. -18.3°C) or 1,1,1,2,2,3,3-heptafluoropropane (R227ca; b.pt. -16.3°C), or a mixture of two or more thereof, in an amount from 30 to 94% by weight based on the weight of the composition and
- (c) an unsubstituted hydrocarbon of the formula C_nH_m in

which n is at least 4 and m is at least $2n-2$, other than methyl propane, in an amount from 1 to 10% by weight based on the weight of the composition.

The present invention also provides a process for producing refrigeration which comprises condensing a composition of the present invention and thereafter evaporating the composition in the vicinity of a body to be cooled. The invention also provides a refrigeration apparatus containing, as refrigerant, a composition of the present invention.

Component (c) will be present in amount from 1 to 10%, especially 1 to 8%, preferably 2 to 6% and more preferably 2 to 5%, and in particular 3 to 4%, most preferably about 3.5%, by weight of the composition.

It will be appreciated that component (a) and component (b) can both be R125. In this situation the composition can, therefore, be binary and the amount of R125 will be from 90 to 99% by weight. In all other situations, the composition will be at least ternary.

Among the preferred compositions of the present invention are those which contain one of more of R125, R134a and R218. Thus component (a) preferably comprises R125 and/or R218 while component (b) preferably comprises R125 and/or R134a.

The presence of R218 (b.pt -36.7°C) is particularly useful where the only other fluorocarbon is R134a. In such circumstances R218 is particularly present in an amount from 5 to 20% by weight, especially 5 to 15%, and more preferably 7 to 12% by weight of the composition.

Component (a) is present in an amount from 5 to 60% by weight, generally 5 to 50% by weight. If R125 does not form part of component (a) then the amount will typically be from 5 to 20%, especially 5 to 15% and preferably 7 to 12%, by weight. It will be appreciated that if the composition contains R125, the concentration of R125 can be split between components (a) and (b).

The concentration of component (b) is from 30 to 94% by weight, generally 50 to 90% and especially 75 to 90%, by

weight.

Typically hydrocarbons which can be employed as component (c), and which may be saturated or unsaturated, possess 4 or 5 carbon atoms and include methylenecyclopropane, 1-butene, cis and trans-2-butene, butane, cyclobutane, cyclopentene, cyclopentane, 2-methyl-1-butene, 2-methyl-2-butene, 3-methyl-1-butene, 1-pentene, cis and trans-2-pentene, 2-methylbutane, pentane and mixtures of two or more thereof. The use of n-butane (R600) is particularly preferred.

Specific formulations which have been found to be effective are as follows:

<u>% by weight</u>		<u>% by weight</u>	
		(a)	(b)
R218	9	R125 46	46.5
R134a	88	50	50
n-butane	3	4	3.5
	100	100	100

The following Examples further illustrate the present invention; Examples 2, 3 and 5 are included for comparison.

Worst case fractionation study:

The apparatus used for these determinations consisted of a small stainless steel cylinder (343 cm³ internal volume) which was charged with the blend under evaluation in various fill ratios and was then placed in a temperature controlled bath brought to the appropriate temperature and allowed to equilibrate for at least 30 minutes. The temperature in the bath was controlled to within 0.1°C and was monitored with a platinum resistance thermometer. Once equilibrated a 75 cm³ sample cylinder was attached to the test cylinder using quick connections and the void spaces between the test cylinder and the sample cylinder evacuated with a vacuum pump. The system was left for at least 15 minutes to check for leaks and then vapour from the test cylinder was slowly introduced into the sample cylinder using a metering valve. Once the pressure in the sample cylinder reached 1 atmosphere the introduction was stopped, the two cylinders isolated and then the sample cylinder was removed for analysis by GLC. The GLC was

calibrated using three separate analyses of a standard which were made up in such a way as to be quite close to the vapour composition expected for the test mixture. This sampling was repeated and a duplicate sample analysed on the GLC. This was repeated at various temperatures with various fill ratios and the worst case result was the one with the highest hydrocarbon content.

The results obtained as shown below. The flammability tests, determined using the method detailed in ASTM E 681-85, show that the formulations of Examples 1 and 4 are significantly superior to those of Examples 2, 3 and 5, while possessing good refrigeration performance. It will be noted that the vapour of the composition of Example 1 (and 4) was non-flammable. It is clear that similar comments apply to the composition R125 - 46.5%, R134A - 50% and R600 - 3.5%.

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	Liquid Composition % w/w					
	R125	R218	R134a	R600a	R600	
Example 1	46	-	50	-	4	100
Example 2	46	-	50	4	-	100
Example 3	46.5	-	50	3.5	-	100
Example 4	-	9	88	-	3	100
Example 5	-	9	88	3	-	100

Refrigeration Performance as an alternative to R22

Evaporator Temperature / °C	Refrigeration Effect / kW				Coefficient of Performance			
	R22	Example 1	Example 2	Example 3	R22	Example 1	Example 2	Example 3
-15	0.932	0.855	0.823	0.711	1.269	1.204	1.184	0.966
-10	1.328	1.124	1.133	1.058	1.492	1.443	1.436	1.323
-5	1.723	1.437	1.478	1.413	1.716	1.700	1.695	1.624
0	2.118	1.796	1.852	1.775	1.939	1.976	1.970	1.869
5	2.513	2.200	2.262	2.145	2.163	2.270	2.262	2.058

Refrigeration Performance as an alternative to R12

Evaporator Temperature / °C	Refrigeration Effect / kW			Coefficient of Performance		
	R12	Example 4	Example 5	R12	Example 4	Example 5
-15	0.585	0.706	0.738	0.942	1.002	1.036
-10	0.786	0.877	0.889	1.227	1.312	1.314
-5	1.018	1.119	1.128	1.513	1.623	1.591
0	1.281	1.434	1.453	1.799	1.933	1.869
5	1.575	1.820	1.865	2.085	2.244	2.148

Fractionation and Flammability test results

Blend	Fractionated Vapour Composition / % w/w					Lower Flammable Limit % v/v in Air
	R125	R218	R134a	R600a	R600	
Example 1	60.7	-	34.6	-	4.7	Non Flammable
Example 2	64.4	-	29.1	6.5	-	12
Example 3	64.7	-	29.8	5.5	-	15
Example 4	-	22.9	72.5	-	4.6	Non Flammable
Example 5	-	21.6	72.5	6	-	9

CLAIMS

- 5 1. A refrigerant composition which comprises:
- (a) pentafluoroethane, octafluoropropane,
trifluoromethoxydifluoromethane or hexafluoro-cyclopropane,
or a mixture of two or more thereof, in an amount from 5 to
60% based on the weight of the composition,
- 10 (b) pentafluoroethane, 1,1,1,2- or 1,1,2,2-
tetrafluoroethane, 1,1-difluoroethane,
trifluoromethoxypentafluoroethane, 1,1,1,2,3,3,3-
heptafluoropropane or 1,1,1,2,2,3,3-heptafluoropropane, or a
mixture of two or more thereof, in an amount from 30 to 94%
15 by weight based on the weight of the composition and
- (c) an unsubstituted hydrocarbon of the formula
 C_nH_m in which n is at least 4 and m is at least $2n-2$, other
than methyl propane, in an amount from 1 to 10% by weight
based on the weight of the composition.
- 20 2. A composition according to claim 1 in which
component (c) is present in an amount from 2 to 6% by weight
based on the weight of the composition.
3. A composition according to claim 2 in which
component (c) is present in an amount from 3 to 4% by weight
25 based on the weight of the composition.
4. A composition according to any one of the
preceding claims which contains one or more of
pentafluoroethane, 1,1,1,2-tetrafluoroethane and

octafluoropropane.

5. A composition according to any one of the preceding claims in which component (a) and (b) are both pentafluoroethane which is present in an amount from 90 to 99% by weight based on the weight of the composition.

6. A composition according to any one of the preceding claims in which component (a) comprises octafluoropropane and component (b) is 1,1,1,2-tetrafluoroethane.

7. A composition according to claim 6 in which the octafluoropropane is present in an amount from 5 to 15% by weight based on the weight of the composition.

8. A composition according to claim 7 in which the octafluoropropane is present in an amount from 7 to 12% by weight based on the weight of the composition.

9. A composition according to any one of the preceding claims which comprises from 5 to 20% by weight based on the weight of the composition of pentafluoroethane.

10. A composition according to any one of the preceding claims in which component (b) is present in an amount from 75% to 90% by weight based on the weight of the composition.

11. A composition according to any one of the preceding claims in which component (c) possesses 4 or 5 carbon atoms.

12. A composition according to claim 11 in which component (c) is n-butane.

13. A composition according to claim 1 specifically

identified herein.

14. A composition according to claim 1 substantially as hereinbefore described.

5 15. Use of a composition as claimed in any one of the preceding claims as a refrigerant in a refrigeration apparatus.

10 16. The process for producing refrigeration which comprises condensing a composition as claimed in any one of claims 1 to 14 and thereafter evaporating the composition in the vicinity of a body to be cooled.

17. A refrigeration apparatus containing, as refrigerant, a composition as claimed in any one of claims 1 to 14.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 98/02079

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09K5/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	GB 2 247 462 A (STAR REFRIGERATION) 4 March 1992 see page 4, line 14 - page 5, line 22 see claims 1-4,6,7 ---	1-5, 11-17
A	EP 0 565 265 A (STAR REFRIGERATION) 13 October 1993 see claims 1,16,17; examples 1,2 --- -/--	1,4,6-8, 11-17

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance
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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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